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(54) **Surface treatment method for titanium or titanium alloy.**

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Description

This invention relates to a method of treating the surface of titanium or a titanium alloy (hereinafter titanium or a titanium alloy is simply referred to as a titanium alloy) to obtain a titanium alloy that can be used in parts sliding with other types of metals.

In general, various types of metal materials are used, for example, in engine parts for a vehicle. Heretofore, some of these engine parts have been made from titanium alloys which are smaller in specific gravity than steel materials, thereby reducing the weight of the entire engine. However, when parts made of titanium alloys which are not processed by a special surface treatment are used in parts sliding with other types of metals, the titanium alloy parts tend to cause burning with other metals or undergo considerable abrasion. In order to prevent this, titanium alloy parts have been surface treated by nitriding, cementation, or plating.

However, when a titanium alloy part is surface treated such as by nitriding, hardness of the part is remarkably increased, which tends to increase abrasion of a metal part sliding with the titanium alloy part. When the surface of a titanium alloy part is plated, the coating layer tends to peel during sliding with partner metal parts, thus posing a reliability problem. Therefore, development of a low-cost and reliable surface treatment method has been in demand.

GB-A-2 118 978 relates to a method of forming an oxide layer on titanium, wherein a work piece is heated in an oxidative atmosphere to a temperature between 500° C and 900° C in order to obtain an oxide layer which comprises a uniform mixture of Ti_2O_3 and Al_2O_3 having a composition of $(Ti, Al)_2O_3$.

SU-A-01 046 342 discloses a thermochemical treatment of titanium alloy products, wherein the oxidation temperature is between 1,050° C and 1,060° C. However, at temperature exceeding 1,050° C, titanium alloy crystal grains become coarse, resulting in deteriorated mechanical properties.

JP-A-62-149 859 discloses a method of producing β -type titanium alloy wire, wherein the oxidation temperature is between 400° C and 650° C. However, at temperatures below 700° C, the surface hardness has insufficient abrasion resistance.

JP-A-63-235 460 discloses a method for producing β -type titanium alloy forged products, wherein the oxidation temperature is between 600° C and 750° C and oxidation time is between 10 and 60 minutes. At temperatures of 700 to 750° C, heating for 9 to 10 hours is required to obtain a hardened layer having a sufficient abrasion resistance. Therefore, the oxidation time according to this reference is too short to obtain sufficient hardness of the work piece.

With a view to eliminate the above prior art problems of surface treatment methods for a titanium alloy, it is a primary object of the present invention to provide a method for treating the surface of a titanium alloy that improves burning resistance and abrasion resistance of the titanium alloy and prevents abrasion of a partner part sliding with the titanium alloy from increasing, thereby improving durability.

This object is met by the invention as set out in claim 1.

When the workpiece is subjected to the oxidation treatment comprising the heating and the descaling, an oxide film formed by the oxidation treatment provides close adhesion to the titanium alloy, thereby obtaining improved abrasion resistance. Thus, abrasion resistance and burning resistance of the titanium alloy part are improved as compared with the case of only the oxidation treatment process, and abrasion of a partner part sliding with the titanium alloy part is prevented from increasing, thereby improving the durability.

According to a preferred embodiment of the invention, after descaling the workpiece, it is subjected to an aging process by maintaining the workpiece at a predetermined temperature.

By subjecting the workpiece to the oxidation treatment after cleaning and then to the aging treatment, abrasion resistance and burning resistance of the workpiece can be even further improved, and abrasion of a partner part sliding with the titanium alloy part is prevented from increasing, thereby improving the durability.

Brief Description of the Drawings

Fig.1 is a graph showing results of motoring durability tests of a valve spring retainer of embodiments.

Fig.2 is a schematic cross sectional view showing structure of a valve mechanism of an engine in the embodiments.

Fig.3 is a graph showing relationship between heating temperature and surface hardness.

Figs.4, 5 and 6 are schematic cross sectional views showing structures of oxide films with different heating temperatures of the heating process.

Fig.7 is a phase diagram in the embodiments.

Fig.8 is a graph showing relationship between distance from the surface and hardness in the embodiments.

Detailed Description of Preferred Embodiments

Fig.2 is a schematic view showing part of a valve mechanism 1 of an engine, wherein numeral 2 denotes a valve member of an intake valve or exhaust valve. A valve spring retainer 4 is mounted to an upper end of a valve stem 3 of the valve member 2. An upper end of a valve spring 5 disposed around the valve stem 3 of the valve member 2 is pressed against a valve spring retainer 4. In this case, the valve spring 5 is made of, for example, a steel material, and the valve spring retainer 4 is made of titanium or a titanium alloy, for example, a Ti-22V-4Al alloy, which is a β -type titanium alloy.

Other types of metals to which the surface treatment method of the present invention can be applied include pure titanium which is an α -type metal; Ti-5Al-2.5Sn which is an α -type titanium alloy; Ti-5Al-6Sn-2Zr-1Mo-0.2Si, Ti-8Al-1Mo-1V, and Ti-6Al-2Sn-4Zr-2Mo which are near- α -type titanium alloys; Ti-6Al-4V, Ti-6Al-6V-2Sr, Ti-6Al-2Sn-4Zr-6Mo, and Ti-8Mn which are $\alpha + \beta$ -type titanium alloys; Ti-13V-11Cr-3Al, Ti-8Mo-8V-2Fe-3Al, Ti-3Al-8V-6Cr-4Mo-4Zr (called β C), and Ti-11.5Mo-6Cr-4.5Sn (called β III). An example using the valve spring retainer 4 as a workpiece to be surface treated will be described below.

Embodiment 1

The valve spring retainer 4 was pretreated by ultrasonically cleaning in hydrochloric acid for 10 minutes.

This pretreatment is to remove impurities such as oil films and oxides from the surface of the titanium alloy, and a positive cleaning effect is achieved by the use of the ultrasonic cleaning in hydrochloric acid or nitric acid.

After the pretreatment process, the valve spring retainer 4 was subjected to oxidation treatment by heating for 30 minutes in an oxidative atmosphere, e.g., in the atmosphere at a temperature of 900 °C to form a composite layer comprising oxide layers and oxygen-enriched layers on the surface of the workpiece (heating process), and then rapidly quenching with water to remove a scale layer of a surface composite layer of the workpiece (descaling process).

The heat treatment in the heating process is not limited to the above conditions. If the heating temperature is lower than 700 °C, hardness (Vickers) Hv of the workpiece is lower than 500 as shown in Fig.3, resulting in a low abrasion resistance. If the heating temperature is higher than 1,050 °C, crystal grains of the titanium alloy formed on the surface of the object material tend to be coarse, resulting in decreases in tensile strength and fatigue resistance and an excessive increase in weight after treatment. The heating time set longer at a lower heating temperature (e.g. 700 °C for a period of 10 hours) and shorter at a higher heating temperature (e.g. at 1,050 °C for 5 minutes), thereby obtaining the same effect as with the above embodiment. In the above embodiment, after the heating process, the workpiece is quenched by water cooling but, alternatively, it may be cooled by air. The cooling water is typically at room temperature of around 20 °C but may be at temperatures of below 80 °C. Using such cooling water, the workpiece is cooled down to near room temperature, typically in about 1 minute. When air-cooled, the workpiece may be allowed to stand until it is cooled to an ambient temperature, or, may alternatively be forcedly cooled to the ambient temperature by blowing a gas such as air, nitrogen, or argon onto the workpiece.

Different heating temperatures in the heating process result in differences in the structure of the oxide films formed on the surface of the titanium alloy.

Figs.4, 5 and 6 show examples of different structures of oxide film on titanium 11 due to different heating temperatures in the heating process. Fig.4, 5 and 6 show the structures of oxide films produced at heating temperatures of 700 to 800 °C, 825 to 850 °C, and 875 to 1,050 °C, respectively. In the case of Fig.4, a single TiO₂ (rutile) layer 12 is formed on the surface of bronze-colored titanium 11. In the cases of Figs.5 and 6, composite layers 13 and 14, respectively, comprising a plurality of oxide layers and oxygen-enriched layers are formed on the surface of titanium 11. The composite layer 13 shown in Fig.5 comprises, from the inner side, a I-layer 13a comprising a titanium + TiO₂ powder layer, a II-layer 13b comprising a TiO₂ + metallic titanium layer, a III-layer 13c comprising a dark blue TiO₂ layer, a IV-layer 13d comprising a light blue TiO₂ layer, and a V-layer 13e comprising a yellow-brown TiO₂ layer. The composite layer 14 shown in Fig.6 comprises, from the inner side, a I-layer 14a comprising a titanium + TiO₂ powder layer, a II-layer 14b comprising a TiO₂ + metallic titanium layer, a III-layer 14c comprising a TiO₂ layer, a IV-layer 14d comprising a Ti₂O₃ layer, and a V-layer 14e comprising a dark blue TiO₂ layer.

Test results of surface hardness of a workpiece comprising a Ti-22V-4Al alloy treated in Embodiment 1 (pretreatment + oxidation treatment) in comparison with those of a workpiece (Comparative Example 1) subjected only to the oxidation treatment (not pretreated) are shown below.

Surface hardness	Hv (0.025)
Comparative Ex. 1 (not pretreated)	576, 641, 678, 686
Embodiment 1 (pretreated)	641, 651, 672, 706

As shown above, the workpiece of Embodiment 1 which is oxidation treated after pretreatment shows higher surface hardness than Comparative Example 1. This is considered as due to the fact that adhesion of the oxide film to the titanium alloy is improved.

The oxidation treatment in the above embodiment is that after the heating process, the workpiece is quenched to remove an external oxide scale layer comprising a porous oxide at the outermost layer of the surface composite layer 13. Thus, a hardened layer having almost the same hardness as the valve spring 5 side sliding with the valve spring retainer 4 can be formed to a relatively large thickness (e.g., 100 μm or more) on the surface of the valve spring retainer 4, thereby improving the burning resistance and abrasion resistance of the Ti-22V-4Al alloy part and preventing an increase in abrasion of the valve spring 5 side sliding with the Ti-22V-4Al alloy part, with improved durability.

Embodiment 2 (Not according to the invention)

The valve spring retainer 4 as a workpiece which was not pretreated was subjected to oxidation treatment by heat treating (heating process) followed by rapidly quenching to remove a scale layer as the outermost layer of the surface composite layer (descaling process), as in Embodiment 1.

After the oxidation treatment, the workpiece was aged by maintaining at 500 °C for 2 hours.

By the heat treatment at 900 ° in the oxidation treatment, the workpiece wholly becomes a β -phase, as shown in Fig. 7. That is, a solution treatment is also made by the heat treatment. After that, by maintaining at 500 °C, an α -phase deposits, which is harder than the β -phase, thus achieving aging.

Aging is referred to maintaining at a constant temperature for a predetermined period of time to deposit the α -phase. For the titanium alloy (Ti-22V-4Al) in the above embodiment, aging is accomplished at a temperature of 450 to 550 °C. Depending on the strength required for the workpiece, the aging is accomplished in 1 to 10 hours.

Embodiment 3

The workpiece was pretreated and oxidation treated as in Embodiment 1, and then aged as in Embodiment 2.

Effects of aging were confirmed by comparing the object material of this embodiment with that of Embodiment 1.

The following table shows the values of surface hardness and core hardness. As can be seen, hardness of the object material is further improved by the aging, which leads to improved abrasion resistance as will be described later.

	Surface hardness HV (0.025)	Core hardness HV (10)
Comp. Ex. 2 (untreated)	262	274
Embodiment 1 (unaged)	669	226
Embodiment 2 (aged)	704	352

Fig.8 shows experimental results of the relationship between the distance from the surface and hardness (hardness distribution) on a workpiece which was pretreated and oxidation treated as in Embodiment 1 and a workpiece which was subjected to the pretreatment, oxidation treatment, and aging in Embodiment 3.

Comparative Tests

The valve spring retainers 4 of Embodiment 1 (pretreatment + oxidation treatment), Embodiment 2 (oxidation treatment + aging), and Embodiment 3 (pretreatment + oxidation treatment + aging) were subjected to motoring durability tests to measure an abrasion Δt of a seat face 5a of the valve spring 5 in the valve spring retainer 4. The results are shown in Fig.1.

For comparison, Comparative Test 1 which was treated only by the oxidation treatment without pretreatment and Comparative Test 2 which was untreated were also subjected to the same Tests.

From Fig.1, it is noted that abrasion resistance is improved by pretreatment (Embodiment 1) or aging (Embodiment 2) as compared with Comparative Test 1 which is only oxidation treated, and abrasion resistance is further improved by both pretreatment and aging (Embodiment 3).

The aging temperature, that is, a temperature at which the α -phase deposits, varies with the type of the titanium alloy, and it is necessary to use a temperature suitable for the specific titanium alloy. For example, as in the above embodiment, the β -type Ti-13V-11Cr-3Al alloy is aged at 426 to 482 °C, the Ti-3Al-8V-6Cr-4Mo-4Zr (β C) alloy is aged at 375 to 475 °C, the $\alpha + \beta$ -type Ti-6Al-4V alloy is aged at 482 to 538 °C, the Ti-6Al-6V-2Sr alloy is aged at 482 to 648 °C, the Ti-8Mn alloy is aged at 482 to 510 °C, and the near- α -type Ti-8Al-1Mo-1V alloy is aged at 560 to 620 °C. As described above, the aging time, although depending on the strength required, is typically 1 to 10 hours.

In the above-described embodiments, the present invention is applied to the valve spring retainer 4.

Claims

1. A method for treating the surface of titanium or a titanium alloy comprising:
 pretreating a titanium or a titanium alloy workpiece by cleaning it with an acid,
 heating said pretreated workpiece to a temperature of 825 °C to less than 1,050 °C in an oxidative atmosphere for a predetermined period of time to form a composite layer comprising oxide layers and oxygen-enriched layers on the surface of said workpiece, and
 rapidly quenching said workpiece to remove a scale layer formed as an outermost layer of said composite layer on the surface of the workpiece.
2. The method of claim 1, further comprising aging by maintaining said workpiece at a predetermined temperature.
3. The method of claims 1 or 2, wherein the heating time is shorter at a higher heating temperature and longer at a lower heating temperature.

Patentansprüche

1. Verfahren zur Behandlung der Oberfläche von Titan oder einer Titanlegierung, umfassend:
 Vorbehandeln eines Titan- oder Titanlegierungswerkstücks durch Reinigung mit einer Säure,
 Erwärmen des vorbehandelten Werkstücks auf eine Temperatur von 825 °C bis zu weniger als 1050 °C in einer oxidierenden Atmosphäre für einen vorgegebenen Zeitraum zur Bildung einer Verbundschicht, die Oxidschichten und sauerstoffangereicherte Schichten auf der Oberfläche des Werkstücks umfaßt, und
 schnelles Abschrecken des Werkstücks zur Beseitigung einer Schlackenschicht, die als äußerste Schicht der Verbundschicht auf der Oberfläche des Werkstücks gebildet ist.
2. Verfahren nach Anspruch 1, weiterhin umfassend einen Alterungsvorgang durch Halten des Werkstücks auf einer vorgegebenen Temperatur.
3. Verfahren nach Anspruch 1 oder 2, wobei die Erwärmungszeit bei einer hohen Erwärmungstemperatur kürzer und bei einer niedrigeren Erwärmungstemperatur länger ist.

Revendications

1. Procédé de traitement de surface de titane ou d'un alliage de titane comprenant :
 le pré-traitement d'une pièce en titane ou en un alliage de titane par nettoyage à l'aide d'un acide,
 le chauffage de ladite pièce pré-traitée à une température de 825 °C à moins de 1050 °C dans une

atmosphère oxydante pendant une durée prédéterminée pour former une couche composite comprenant des couches d'oxyde et des couches enrichies en oxygène sur la surface de ladite pièce et

la trempe rapide de ladite pièce pour retirer une couche de calamine formée en tant que couche la plus extérieure de ladite couche composite sur la surface de la pièce.

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2. Procédé selon la revendication 1, comprenant en outre le vieillissement par maintien de ladite pièce à une température prédéterminée.

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3. Procédé selon les revendications 1 ou 2, dans lequel la durée de chauffage est plus courte à une température de chauffage élevée et plus longue à une température de chauffage inférieure.

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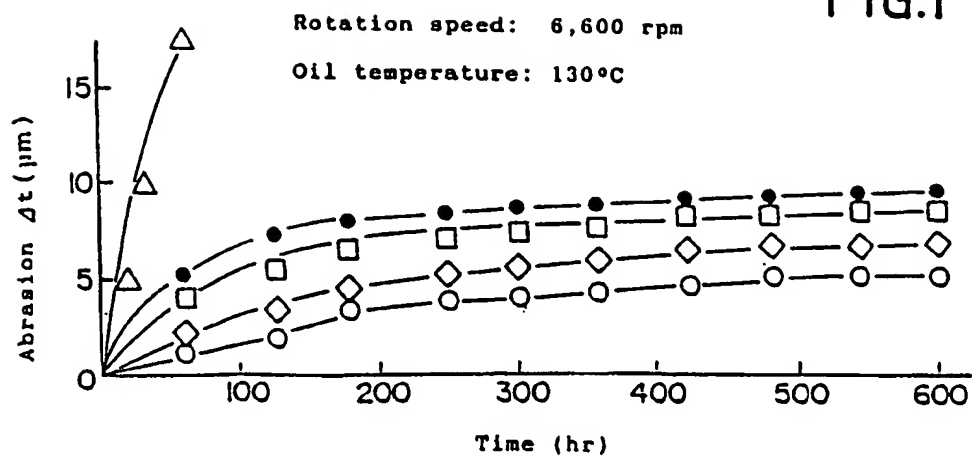
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FIG.1



- Δ Comparative Example 2 (untreated)
- Comparative Example 1 (oxidation treatment only)
- Embodiment 1 (pretreatment + oxidation)
- ◇ Embodiment 2 (oxidation + aging)
- Embodiment 3 (pretreatment + oxidation + aging)

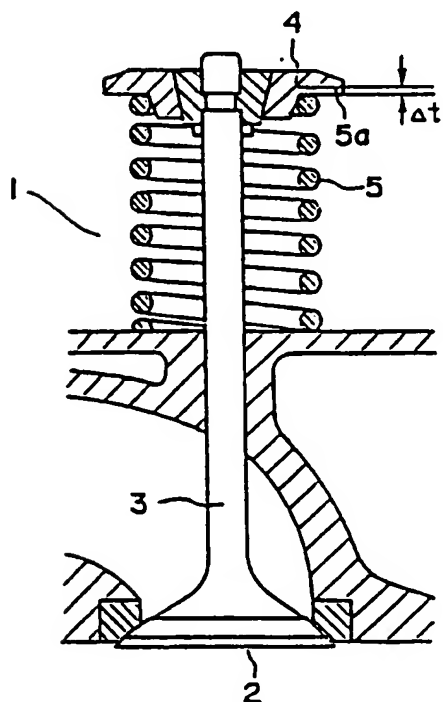


FIG.2

FIG.3

Surface hardness vs. temperature when heated for 30 min

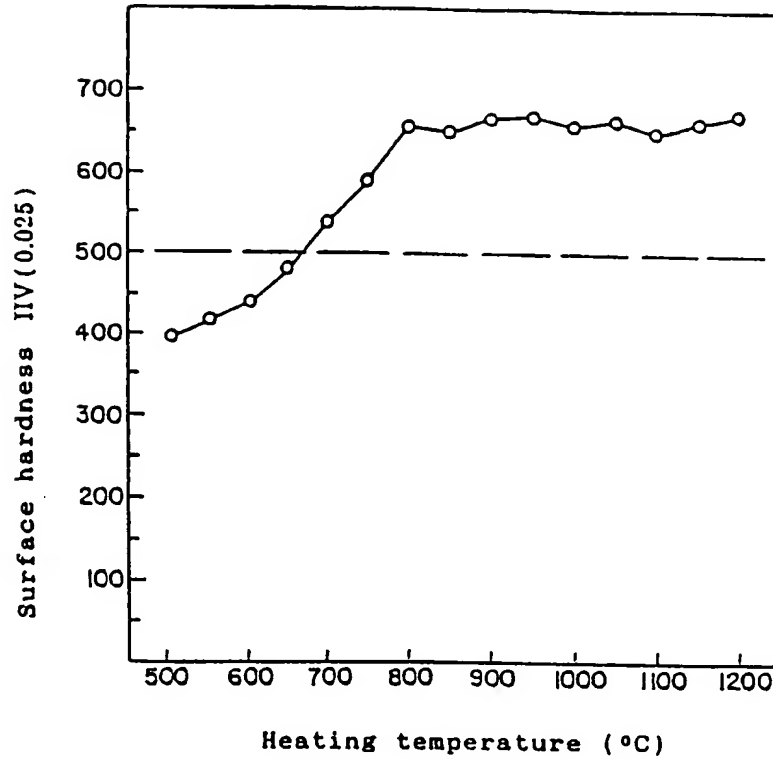


FIG.4

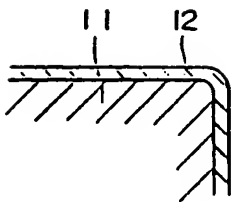


FIG.5

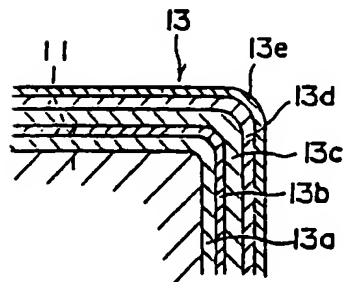
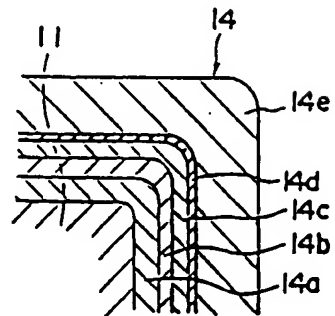


FIG.6



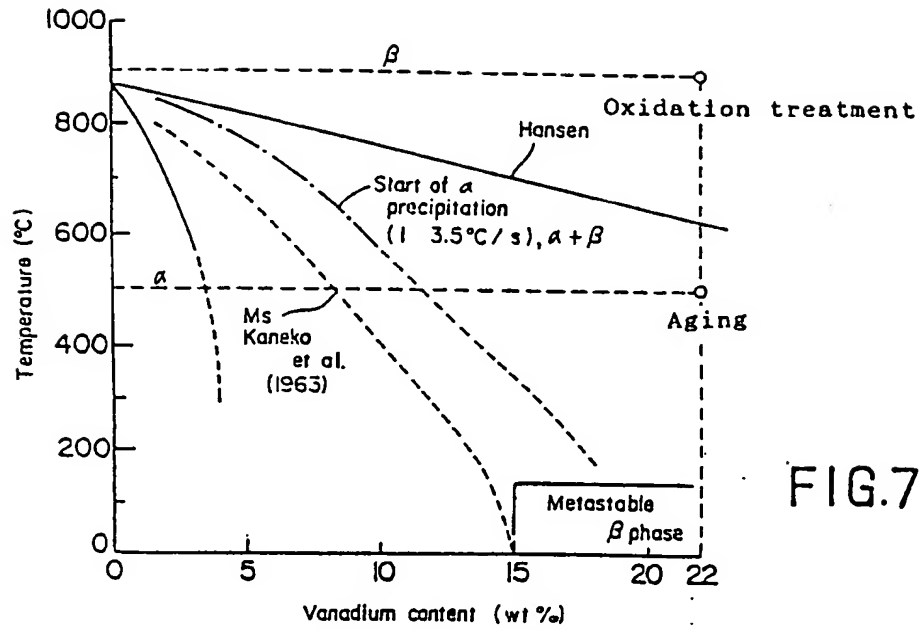


FIG. 7

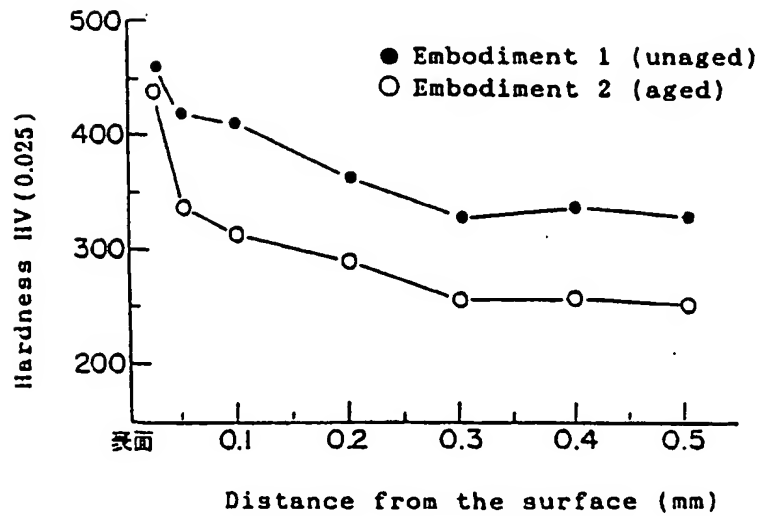


FIG. 8